

SECTION 10

IMPLICATION OF PERCHLORATE CONTAMINATION ON CALIFORNIA'S WATER SUPPLY

I. INTRODUCTION

As a salt, perchlorate exhibits the characteristics of high solubility and mobility in water as well as being very stable. These characteristics lead to the formation of long and persistent contaminant plumes when released into either ground water or surface water. The movement of perchlorate in soil is largely a function of the amount of water present. Perchlorate does not bind to soil particles. Perchlorate salts that are released to the soil in solid form will readily dissolve in whatever moisture is available. If sufficient infiltration occurs, the perchlorate will be completely leached from the soil.¹ In dilute concentrations typically found in groundwater, perchlorate behaves conservatively, with the center of mass of the plume moving at the same average velocity as the water. Biodegradation of perchlorate in groundwater will not occur unless significant levels of organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present.^{1 above}

Perchlorate began to be discovered at various manufacturing sites and in well water and drinking water supplies within the months following the April 1997 development of an ion chromatography analytical method developed by the California Department of Health Services. This new analytical method that was substantially more sensitive and able to achieve a detect limit for perchlorate in water as low as 4 micrograms per liter ($\mu\text{g/L}$). By lowering the previous detection limit from 400 $\mu\text{g/L}$, several new occurrences of perchlorate contamination of drinking water became known statewide.

Analytical results for perchlorate in water is typically reported in micrograms per liter ($\mu\text{g/L}$) or in parts per billion (ppb). One $\mu\text{g/L}$ equals 1 ppb. Soil results are usually reported in parts per million (ppm). One ppm equals 1,000 ppb. For consistency in this report, all data will be in ppb.

Perchlorate was first found in drinking water wells in eastern Sacramento County (up to 260 ppb), near Aerojet General Corporation's facility. Aerojet was treating shallow groundwater to remove volatile organic chemicals. As a result of cleanup, analysis of the groundwater confirmed the presence of perchlorate. It was in response to these findings that DHS established a new analytical method for perchlorate.

In 1997, DHS' sampling occurred in southern California. DHS found perchlorate in a drinking water wells in Los Angeles County, San Bernardino County, and Riverside County. Sampling also showed perchlorate at low levels in Colorado River water, an important source of drinking water and water for agriculture (irrigation) in southern California.

II. EXTENT OF WATER SUPPLY CONTAMINATION

Most of the perchlorate detections in drinking water are found in Southern California. Perchlorate has been detected in groundwater and monitoring wells in and around facilities handling perchlorate in the Los Angeles Region. Drinking water wells in the cities of Alhambra, Arcadia, Azusa, Duarte, San Marino, Commerce, Covina, El Monte, Glendora, City of Industry, La Puente, Pasadena, Pomona, La Verne, Santa Clarita, Los Angeles, Norwalk, Bellflower, Baldwin Park, Monrovia, Monterey Park, San Gabriel, South Pasadena, San Dimas, Vernon and Whittier have detected perchlorate in recent years. Prior to 1997, there were no requirements to test water systems.

Regional Board staffs are working to locate former United States Department of Defense (DOD) contractors and sub-contractors engaged in manufacturing, storing, transporting and disposing of perchlorate. There are also some fireworks manufacturers under scrutiny. To date, six known perchlorate source sites and 15 suspected source sites have been identified. Further site investigations and assessments of the suspected source site will be completed.

As of April 2003, according to the California Department of Health Services, over 173 surface water (springs/reservoirs) and groundwater sampling points within the Los Angeles Region have detected levels of perchlorate (ranging from 4 to 159 ppb). This figure is up from the 150 reported in mid December 2002. The groundwater sampling points involve supply wells, water treatment influent/effluent, irrigation and monitoring wells. Site specific groundwater monitoring has verified a wider impact throughout the Los Angeles Region.

III. REGIONAL WATER QUALITY CONTROL BOARD SITES

Ventura County – Los Angeles RWQCB

Subsurface investigations indicate a perchlorate plume beneath Boeing's Santa Susana Field Laboratory near Simi Valley. This site is located just west of the Los Angeles County/Ventura County borderline. At the SSFL, the highest perchlorate concentration of 1,600 ppb was detected along the eastern part of the facility in the fractured Chatsworth Formation.

Perchlorate has also been detected in two supply wells at the United States Naval facility on San Nicholas Island. It is believed the perchlorate contained in explosive ordinances is the source. There have been no other detections of perchlorate in any other municipal supply wells throughout Ventura County.

Also See Section 9 for Boeing Rocketdyne Santa Susana Field Laboratory and San Nicholas Island information.

Central Groundwater Basin – Los Angeles RWQCB

There have been only five sporadic perchlorate detection's reported in the Central Groundwater Basin. Perchlorate impact on drinking water supply systems has been reported in Vernon, Commerce, Norwalk and Bellflower. Perchlorate concentrations range from 4 to 13 ppb. The source sites are currently unknown.

Raymond Groundwater Basin – Los Angeles RWQCB

Also see
National Aeronautics and Space Administration/Jet Propulsion Laboratories
Pasadena, California

The latest water quality information on perchlorate from the City of Pasadena for December 2002 indicates that they have decided to shut down 9 of their 13 drinking water supply wells due to perchlorate pollution. Twelve other nearby wells are also impacted by perchlorate, bringing the total to 25.

San Gabriel/Pomona Valley – Los Angeles RWQCB

Based on the information provided by DHS for April 2003, 69 water supply wells have become contaminated by perchlorate. Approximately 10 of these wells have been shut down due to volatile organic compound and perchlorate contamination. Federal and State regulatory agencies, municipalities, as well as water supply companies are tracking these events. In August 2002, six of these drinking water wells were taken out of service in South El Monte due to elevated concentrations of perchlorate and volatile organic compounds beyond the already identified. Over 11,500 gallons per minute (gpm) of drinkable water has been temporarily lost due to well shutdowns. All of these wells lie within the South El Monte Operable Unit (SEMOU).

The list of perchlorate-impacted municipal wells continues to grow. Two wells in the City of Industry remain shut down due to elevated perchlorate concentrations. In West Covina, three well have also been shut down.

Pomona Valley – Los Angeles RWQCB

The City of Pomona reports that as many as 23 drinking water wells have detected perchlorate at various times during 2002. Some wells located in the City of Pomona have been taken off-line. These detections, in addition to increasing volatile organic compound concentrations, have caused the shut down of 2 of these 23 drinking water wells. Perchlorate concentrations range from 4 ppb to as high as 19 ppb. To reduce the impact of increasing perchlorate concentrations, the City of Pomona blends impacted groundwater with non-impacted water prior to sending it through their 15 million gallon per day treatment plant.

Santa Clarita Valley/San Fernando Valley – Los Angeles RWQCB

In the Santa Clarita area, perchlorate has impacted a total of 5 wells affecting three water systems (Newhall Community Water District, Valencia Water District, and Santa Clarita Water Company). Perchlorate detected in these wells ranged from 4.2 ppb to 47 ppb. In the San Fernando Valley perchlorate has been detected in a total of 12 wells affecting two water systems (Los Angeles Department of Water and Power and Glendale City Water Department). Perchlorate detected in these wells ranged from 4 ppb to 21 ppb.

San Bernardino County - Santa Ana RWQCB

In the Rialto-Colton area in San Bernardino, perchlorate has been detected in 20 water supply wells at concentrations above the California notification level of 4 ppb. The loss of these wells created a serious water supply shortage in the summer of 2003 for the four affected water companies. EPA has issued a Unilateral Administrative Order to two former operators at the site and the State of California Regional Water Quality Control Board has issued investigation orders to 19 parties suspected of testing, manufacturing, storing, or disposing of perchlorate-containing materials in the area. The state has already provided \$6 million to help the four affected water companies purchase water treatment equipment. One of the Potentially Responsible Parties (PRPs) has provided an additional \$4 million. As of September 2003, the four water utilities have installed four ion exchange systems and by the end of the year four more systems are expected to go online, allowing treatment of more than 20 million gallons per day of perchlorate-contaminated groundwater.

San Gabriel Superfund Site

San Gabriel Superfund Site
Los Angeles
CAD980818579

Site Description:

The San Gabriel Valley Superfund Site is located approximately 10 to 20 miles east of Los Angeles and is considered one of the largest cleanups in the nation. The San Gabriel Valley site includes multiple areas contaminated groundwater in the 167-square-mile San Gabriel Valley. Over 30 square miles of groundwater under the Valley may be contaminated.

Site Contamination:

Volatile organics compounds (VOCs) were first detected in 1979. By 1984, 59 wells were found to be contaminated with high levels of various volatile organic compounds and the US EPA listed the site on the National Priority List. In 1997, perchlorate was discovered in the Baldwin Park area of the basin. The basin's 400 water supply wells

provide approximately 90 percent of the domestic water supply for over one million people. The site has been divided into four distinct areas or operable units to better focus investigative and cleanup efforts. The four areas are 1) El Monte, 2) Baldwin Park, 3) Alhambra, and 4) City of Industry & La Puente (Puente Valley Operable Unit).

Area 1 is the El Monte Operable Unit which includes portions of the cities of El Monte, Rosemead, and Temple City. Land use in the area is mixed industrial, commercial, residential, and undeveloped. In addition to volatile organic compound contaminants, perchlorate, 1-4-dioxane, and NDMA have also been detected.

Area 2 or the Baldwin Park Operable Unit was established in order to address the most highly contaminated groundwater in the San Gabriel Basin. It includes portions of the cities of Azusa, Irwindale, Baldwin Park, and West Covina.

The plume of contaminated groundwater in Area 3, the Alhambra Operable Unit, is over a mile wide and eight miles long. The depth to ground water is 150 to 350 feet, and the groundwater contamination extends from the water table to more than 1,000 feet below the surface. The peak contaminant concentration detected is 38,000 ppb of PCE.

Area 4 runs along San Jose Creek in La Puente and includes most of the City of Industry and portions of the City of La Puente and Walnut. The City of Industry is highly industrialized.

IV. TREATMENT OPTIONS

Treatment options for perchlorate contamination can be broadly categorized into two types of processes: physical removal of the perchlorate from the drinking water, which does not result in the destruction of the anion, and chemical destruction of perchlorate, which reduces the perchlorate anion to chloride anion. Each treatment option employs various technologies, with the most common ones summarized below. Some technologies have already been used with various degrees of success, while others are still under research or at the pilot project stage. For a more in depth discussion of available and developing technologies, please refer to DTSC's report titled "Perchlorate Contamination Treatment Alternatives," available on DTSC's website at www.dtsc.ca.gov.²

Perchlorate is difficult to treat because it is a highly soluble inorganic anion, it absorbs poorly to mineral surfaces and activated carbon, and it has a high activation energy which cannot be overcome by common reducing agents. Due to these difficulties, research is still underway to develop treatment technologies that are economically feasible for large scale application. Available technologies for the removal or destruction of the perchlorate ion can be combined to achieve greater efficiency.

Physical Removal of Perchlorate

Physical removal refers to the process of separating the perchlorate ion from the drinking water. Removal of perchlorate from the ion does not destroy the perchlorate, thus additional steps are needed to destroy the perchlorate and manage the wastes that are generated in the process. A major obstacle to implementation is that removal techniques are generally not selective. Beneficial ions naturally found in water sources are usually removed along with the perchlorate anion. Beneficial anions found in water include: bicarbonate, carbonate, dihydrogen monophosphate, hydrogen orthophosphate, and sulfate.³ Because of the lack of selectivity, physical removal technologies generate brine water that is high in perchlorates and other dissolved solids, and additional steps must be taken to treat and dispose of those wastes.

Available technologies for physical removal of the perchlorate anion include anion exchange, membrane filtration, and electrodialysis. Each of these technologies is discussed in more detail below.

Anion Exchange

This technique works by replacing the perchlorate ion with a harmless ion, such as chloride. The contaminated water is made to flow through a resin that contains a high concentration of the replacement ion. Because the replacement ion in the resin is in much higher concentration than the perchlorate in the water, the perchlorate switches place with the replacement ion in the resin, and the replacement ion is released in the water. Eventually, the resin reaches an equilibrium point where no more perchlorate can be extracted from water; at that point the resin must be "regenerated".

The primary benefit of this technique is that it can be readily implemented. The main drawback is that most commercially available resins are not selective enough for perchlorate. Some resins remove all other anions, before binding perchlorate, making the final water product too corrosive for use in water distribution systems without restoring water hardness. Other drawbacks include the production of brines which are very high in perchlorate and other dissolved solids and necessitate additional steps for proper disposal.^{3 above}

Membrane Filtration

Techniques for membrane filtration include reverse osmosis and nanofiltration. Water is forced through a semi-porous polymer membrane, and dissolved salts, including perchlorates, are unable to penetrate the membrane. To some extent, the membrane can be manufactured to be permeable toward certain anions and not others. However, most of the time, to be efficient in the removal of perchlorate, the membrane has to be made impermeable to most other types of dissolved matter, so the result will be a deionized water. The main drawback is that the membrane can become irreversibly fouled by certain metal compounds or microorganisms that can be present in the water, and necessitate periodic replacement. Other drawbacks include energy requirements and production of large volumes of brine containing perchlorate and other dissolved solvents, which would require subsequent steps to treat and dispose.

Granular Activated Carbon (GAC)

This technology utilizes an adsorbent, in this case granular activated carbon, to remove perchlorate from water.⁴ Water flows through columns packed with granulated activated carbon. Organic pollutants in the water become attracted to, and bind to the surface of the carbon. This technology has been used widely to for the removal of various pollutants from the water. It works best for low solubility, high molecular weight, non-polar, branched compounds. There is limited experience for the application of GAC for the removal of perchlorate from groundwater. Research is currently underway to produce a “tailored carbon” which would be effective in the removal of low levels of perchlorate from the water.

Electrodialysis

With this technique, water is passed through channels of alternating semi-permeable and permeable membranes, while being exposed to an electrical field. This produces alternate channels of nearly deionized water and salty water. The deionized water is used and the salty water is discarded. This technology is still under research to determine if it could be feasible for larger scale implementation.

Chemical Destruction of Perchlorate

For a chemical destruction technique to work, it has to overcome the high activation energy needed to reduce the perchlorate ion to chloride ion. The molecular structure of perchlorate is a tetrahedron, consisting of four atoms of oxygen surrounding a central chlorine atom. The surrounding oxygen atoms have the effect of blocking reducing agents from directly attacking the chlorine.⁵ This explains the chemical stability of the perchlorate anion.

Technologies that aim at destroying the perchlorate anion include biological reduction, chemical reduction, and electrochemical reduction.

Biological Reduction

It is believed that this is the most promising technique for the treatment of perchlorate contaminated water. Bioremediation is already in use for the treatment of contaminated soil. Under the right conditions, certain naturally occurring bacteria are capable of completely degrading perchlorate to chloride ion by using perchlorate as an oxidant (electron acceptor) for metabolism. These microorganisms are abundant in nature and can be found in water, wastewater, sediment, and soil, at concentrations ranging from one to thousands of bacteria per gram of matter.⁶ They possess an enzyme called reductase, which enables them to lower the activation energy of perchlorate, and use perchlorate for metabolism. Perchlorate reducing microbes can also be quickly cultured in the laboratory. They are generally effective at reducing perchlorate in regions with adequate rainfall, in the presence of nutrients (such as acetate or lactate), and under oxygen and nitrate free conditions.⁷

The main drawback posed by biological reduction is that the microorganisms capable of degrading perchlorate prefer oxygen.⁸ If the water contains large amounts of dissolved oxygen, the microorganisms will use the oxygen instead of reducing perchlorate. Moreover some bacteria may be pathogenic to humans, and their use to treat drinking water may be problematic.

Bioremediation can be implemented in situ or ex situ. In situ bioremediation aims at destroying the perchlorate in place without the need for removal. In situ biodegradation can be done by digging trenches, directing water flow to the contaminated area, adding high concentration of organic matter, or by injecting substrates (such as lactate) into the soil. Studies show that this technique was successful at reducing perchlorate from concentrations of 660 parts per million to less than 0.018 parts per million within weeks or months, depending on the project.⁹

Ex situ treatment refers to above ground treatment, which typically takes place in specially engineered vessels called bioreactors. This technology is the most widely used and investigated biological technique for perchlorate reduction, as it appears to be both effective and feasible.^{9 above} Several bioreactor technologies have been developed to treat soil using bacteria.^{6 above} The technology involves the pumping of the contaminated water from the ground into the bioreactors, which contain the bacteria. The bacteria use the perchlorate as nourishment by removing it from the water and degrading it. Some advantages of this technique include simplicity of operation, minimal biosludge production, and cost effectiveness.

Phytoremediation, or degradation by plants, may be another option for the treatment of contaminated soil. Some trees, such as willows, can reduce perchlorate. Although this has no applicability for drinking water, it can have some applicability for contaminated soil, or in-situ land remediation.

Chemical Reduction

As mentioned above, due to the high activation requirement of the reduction reaction of perchlorate, common reducing agents are not effective in reducing perchlorate. Perchlorate can be reduced by chemical agents under laboratory conditions, but research is still underway in this field to develop techniques that could be economically viable.

Electroreduction

Perchlorate can be reduced to chloride using an electric current applied directly to the water by a cathode at high potential. This technology is well established for industries such as metal electroplating or brine electrolysis, but it has not yet been implemented in the potable water industry.^{2 above} In time, ions from the water would associate with the electrode surface. The main drawback is high operation cost due to electricity consumption. There are a number of technical difficulties in implementing this technique, such as electrode corrosion and natural organic matter adsorption to the surface of the electrode.

The table below summarizes the pros and cons of treatment technologies that are most promising:

Physical Removal Technologies		
Treatment Technology	Pros	Cons
Anion Exchange	Existing technology Easily implemented Moderate maintenance Fairly inexpensive	Regeneration/down time Hard to make selective Further steps needed to dispose of waste from regeneration
Membrane Filtration	Existing Technology Highly effective Fast Ideal for point of use treatment	Not selective for perchlorate Maintenance needed Membrane can become fouled Additional steps needed to dispose of concentrate
Electrodialysis	Existing technology Highly effective Fast Ideal for point of use treatment	Operation cost is high due to electricity consumption Membrane can become corrupted Not very selective Additional steps needed to dispose of concentrate
Chemical Destruction Technologies		
Biological Reduction	Selective Fairly fast Low operating cost	Bacteria will use oxygen before perchlorate Some bacteria may be pathogenic Food source is needed for

Physical Removal Technologies		
Treatment Technology	Pros	Cons
		bacteria Moderately/high monitoring and maintenance Insufficiently developed at this time Difficult to implement in existing facilities with high output.
Electroreduction	No waste products Low maintenance	High operating cost due to electricity consumption Worker safety is a concern Insufficiently developed at this time Difficult to implement in existing facilities with high output.

Source: Adapted from Urbansky, 1999.

V. ESTIMATED COST OF TREATMENT OPTIONS

In general, estimating the overall cost of each treatment option is difficult because cost can depend on the individual site and its specifics. Factors that play a role in the cost determination include: geology, concentration of perchlorate, evidence of other contaminants, chemical parameters such as pH, alkalinity, and total dissolved solids, and the presence of perchlorate reducing microbes. Thus overall estimated cost has to be adjusted depending on each site. ^{9 above}

The data in the table below was compiled by Harding Lawson Associates (HLA) for the Baldwin Superfund Site Groundwater Operable Unit (California). It provides estimated costs for several treatment methods (some of which are not discussed in this report). The table was originally adapted from the HLA draft report and is cited in several sources, including the one reviewed for purposes of this report. The table has been sorted to list the least expensive technologies first, and it is noted that biological treatment and ion exchange technologies are currently the least expensive.

Treatment Method	Total Capital Cost	Annual Operation and Maintenance Cost	Total Annual Treatment Cost		Normalized Treatment Cost
	(\$ Million)	(\$ Million)	(\$ Million)	(\$/gallon)	
Ion Exchange	28	5.5	10.4	0.95	1.6
Biological Treatment with GAC/FB	35	3	6.6	0.6	1

Treatment Method	Total Capital Cost	Annual Operation and Maintenance Cost	Total Annual Treatment Cost		Normalized Treatment Cost
	(\$ Million)	(\$ Million)	(\$ Million)	(\$/gallon)	
Liquid Phase GAC	46	16	20.7	1.88	3.1
Reverse Osmosis	65	10	16.6	1.52	2.5
Electrodialysis	84	5	13.6	1.06	2.1
Capacitative Deionization	131	3	16.6	1.52	2.5
<p>Total annual treatment cost is determined by adding annual operation and maintenance cost and total capital cost, amortized over 20 years at 8%.</p> <p>All costs are in 1997 dollars</p> <p>All costs are accurate to within plus or minus 50%</p> <p>Cost of land and related environmental requirements are not included.</p>					

Source: Risk Assessment Corporation, 2003; citing to Catts, 1997.

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- ¹ Best, E. P. H., S. L. Sprecher, S. L. Larson, and H. L. Fredrickson. 1998. Environmental Behavior and Fate of Explosives from Groundwater from the Milan Army Ammunition Plant in Aquatic and Wetland Plants: Fate of TNT and RDX. SFIM-AEC-ET-CR-97060. Prepared for the U.S. Army Environmental Center by the U.S. Army Engineer Waterways Experiment Station, Environmental Laboratory, Vicksburg, Miss.
- ² California Environmental Protection Agency, Department of Toxic Substances Control. 2004. *Perchlorate Contamination Treatment Alternatives*. Available at: <http://www.dtsc.ca.gov/HazardousWaste/Perchlorate/index.html>
- ³ Urbansky, E.T., Schock, M.R. 1999. *Issues in Managing the Risks Associated with Perchlorate in Drinking Water*. Journal of Environmental Management. 56, 79-95. Available at: <http://clu-in.org/download/contaminantfocus/perchlorate/urbansky1.pdf>
- ⁴ Risk Assessment Corporation. 2003. *Perchlorate in Groundwater*. Final Report of the Risk Assessment Corporation study on Risk Analysis, Communication, Evaluation, and Reduction at LANL. RAC Report No. 1-RACER LANL-2003-FINAL. Available at: <http://www.racteam.com/LANLRisk/Reports/PerchlorateFinal.pdf>
- ⁵ U.S. Environmental Protection Agency, Technology Innovation Program website. 2005. *Contaminant Focus: Perchlorate, Treatment Technologies*. <http://www.clu-in.org/contaminantfocus/default.focus/sec/perchlorate/cat/Overview/>
- ⁶ Logan, B.E. 2001. *Assessing the Outlook for Perchlorate Remediation*. Environmental Science and Technology. 35(23), 482A- 487A. Available at: <http://pubs.acs.org/subscribe/journals/esthag-a/35/i23/logan/23logan.html>
- ⁷ Urbansky, E.T., Brown, S.K., Magnuson, M.L., Kelty, C.A. 2001. *Perchlorate Levels In Samples of Sodium Nitrate Fertilizer Derived from Chilean Caliche*. Environmental Pollution, 112, 299-302. Available at: <http://www.clu-in.org/download/contaminantfocus/perchlorate/EPCIO4.pdf>
- ⁸ Urbansky, E.T. 2002. *Perchlorate as an environmental contaminant*. Environ. Sci. Pollut. Res. Int. 9 (3), 187 - 92. Available at: http://clu-in.org/download/contaminantfocus/perchlorate/ESPR_9_187_192.pdf
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